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COMPLETE SPECIFICATION.

A Process for Desulphurising Liquid Hydrocarbons.

We, DEUTSCHE GOLD-UND SILBER-SCHEIDEANSTALT VORMALS ROESSLER, 9 Weissfrauenstrasse, Frankfurt (Main), Germany, a Body Corporate organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for desulphurising hydrocarbons.

It is known that sulphur compounds undergo changes on being treated with metallic sodium or with sodium alloys and can also lose their sulphur. Finely dispersed sodium is particularly reactive and this has been proposed as a preferred substance for the desulphurising of mineral oil products.

A most advantageous process for the desulphurising of hydrocarbons is one which only removes the sulphur but not the hydrocarbon radicals of the sulphur compound. When using sodium, this means that the sulphur is present as sodium sulphide after the treatment, whereas the hydrocarbon radicals originally combined with the sulphur remain in chemically changed form with the main quantity of the desulphurised hydrocarbon mixture. In contrast to this condition, most of the conventional desulphurising processes (with the exception of hydrogenation) which are usual in the mineral oil art remove all the organic sulphur compounds, that is to say, also remove the organic residues combined with sulphur.

The sulphur compounds existing in mineral oils show a differential reactivity with respect to sodium. Mercaptans react readily with sodium with the formation of mercaptide. The sodium mercaptides formed are sparingly soluble in hydrocarbons, so that the reaction products which precipitate can be filtered or centrifuged off. However, this method does not lead to a complete desulphurisation and consequently the sodium treatment is followed by a treatment with sulphuric acid. The sulphur remaining in the mineral oil product originates from small quantities of dissolved mercaptide. The removal of the sodium mercaptide by washing with water is not possible, since in this way a hydrolysis equilibrium is set up with formation of sodium hydroxide and reformation of mercaptan. The further reaction of sodium with sodium mercaptide or the thermal treatment of the mercaptide does not lead to the conversion of the sulphur into sodium sulphide.

As shown by experiment, mixtures of hydrocarbons and sodium mercaptides remain unchanged on heating for 10 hours to 260° C., even in the presence of an excess of sodium.

It has now been found that the formation of sodium sulphide from sodium mercaptides is readily possible in the presence of organo-sodium compounds. It is possible to proceed in such a way that the organo-sodium compound is added or is even produced in the reaction mixture. The most simple procedure is to produce the organo-sodium compounds in the reaction mixture by reacting organic halogen compounds with sodium; it is possible to employ aliphatic, cycloaliphatic, aromatic or mixed aliphatic-aromatic halogen compounds.

Moreover, with many other sulphur compounds, the conversion of the organically combined sulphur into sodium sulphide is not possible with sodium alone. It has for example been found that tetraphenyl thiophene, dibenzothiophene, aliphatic disulphides, aliphatic polysulphides and aliphatic

sulphides, on being treated with sodium at temperatures up to 250° C., do not or only incompletely give off their sulphur as sodium sulphide. In the presence of organo-sodium compounds, on the contrary, a reaction in the required form, that is to say, conversion of the sulphur into sulphide, was achieved in all cases.

The sodium sulphide forming in the process according to the invention can be removed by centrifuging, filtering or, in contrast to the hitherto usual procedure, by washing with water. After washing with water, all the sulphur is found as sodium sulphide in the aqueous phase.

The process can be used for desulphurising crude oils, mineral oil products, coking plan products and synthetic hydrocarbons. In combination with other desulphurising processes, it is suitable for removing residual traces of sulphur.

The invention is further illustrated by the following examples:—

Examples.

The reactions are carried out in a heatable four-necked flask with a stirrer device, dropping funnel (with equalisation of pressure relative to the reaction flask), thermometer and reflux condenser (sealed by a dry tube).

(1) Desulphurisation Carried Out Preparing the Organo-Sodium Compound In Situ.

(*a*) *Desulphurisation of solutions containing heptanethiol and hexanethiol:*—

To 250 cc. of a solution of the mercaptan in hydrocarbons (heavy benzine, boiling limits 150 to 195° C., white oil, boiling limits 250 to 315° C.), with a sulphur content of 1.07% there was added at room temperature and while stirring the quantity of sodium dispersed in heavy benzine or white oil which was sufficient to form sodium mercaptide with all the mercaptan present. Such a quantity of halogen compound was introduced dropwise into the stirred mercaptide suspension that the molar ratio between sulphur compound and halogen compound was 1:1. The reaction mixture was heated to a temperature of from 50 to 60° C., and more sodium dispersion was added until the molar ratio between halogen compound and sulphur was 1:2.2. The temperature was raised while stirring to 120° C., and this temperature was maintained for another 30 minutes. Typical discolourations to deep blackish-blue occurred in the reaction. After cooling, methanol was added to fix any unreacted sodium; the mixtures were then washed with water and the discolouration disappeared. After this treatment, the benzine layer was free from sulphur. The sulphur was found in the aqueous phase as sodium sulphide and could be determined by iodometric methods.

The conversion was checked using chlorobenzene, benzyl chloride, butyl chloride, bromobenzene, butyl bromide and cyclohexyl bromide.

(*b*) *Desulphurisation of solutions containing n-heptysulphide, n-heptyl disulphide, amyl polysulphide and dimethyl thiophene:*

First of all bromobenzene, and then a sodium dispersion were added at room temperature with stirring to 250 cc. of a solution of the sulphur compounds in hydrocarbons (heavy benzine, white oil). The solution had a sulphur content of 1.07%). The ratio between sulphur compound, bromobenzene and sodium was so chosen that there was 1 mol of bromobenzene and 3 gram-atoms of sodium to 1 gram-atom of sulphur. The mixture was heated to 120° C., and stirred for 30 minutes at this temperature. The reaction product was worked up, as described under (*a*).

In all cases, a 100% desulphurisation was achieved, whereas with the compounds referred to under (*a*) and (*b*), without addition of a halogen compound, only some of the sulphur was converted into sodium sulphide, even with longer reaction times (up to 10 hours); with the mercaptans, the conversion was up to 20%. while with the substances indicated under (*b*), the conversion in the most favourable case (with the polysulphides) was up to 60%.

(*c*) Solutions of tetraphenyl thiophene and dibenzothiophene remained completely unchanged when treated only with sodium. By using bromobenzene or butyl bromide according to (*b*), a complete desulphurisation was achieved.

(*d*) The following sulphur compounds were dissolved, in different proportions, in 250 cc. of white spirit, so that in all cases a total sulphur content of 2.7% was obtained: hexanethiol, tetrahydrothiopyrane, benzyl mercaptan, heptyl disulphide, phenylethyl sulphide, tetraphenyl thiophene, thionaphthene, dibenzothiophene, thiophenol.

Each solution was reacted according to (*b*). The ratio between sulphur, halogen compound and sodium was so chosen that 1 mol of halogen compound and 3 gram-atoms of sodium were used to 1 gram-atom of sulphur.

A 100% desulphurisation was achieved. It can be shown that desulphurisation was not complete if the addition of halogen compound is omitted.

(2) Desulphurisation Carried Out by Adding a Prepared Organo-Sodium Compound.

(*a*) *Desulphurisation with sodium phenyl:*

250 cc. of a 0.1 molar suspension of

sodium heptyl mercaptide in xylene were added to a 0.1 molar solution of sodium phenyl in xylene. On heating to 120° C., the mixture became deep brown in colour after 10 minutes. Stirring was continued for another 30 minutes at 120° C., and working up was carried out according to (1*a*). The hydrocarbon phase was free from sulphur.

(*b*) *Desulphurisation with sodium cyclopentadienyl*:—

A dispersion of 1.4 g. of sodium in heavy bezine was added dropwise at room temperature to a solution of 3.7 g. of cyclopentadiene in 250 cc. of heavy benzine while stirring; the organic sodium compound flocculated out. 6.6 g. of hexyl mercaptan and thereafter another 1.4 g. of sodium in dispersed form were added. The mixture was heated while stirring to 120° C. and this temperature was maintained for 30 minutes, the contents of the flask becoming blackish-brown in colour. After working up in the usual way, the organic phase was free from sulphur.

(3) Desulphurisation of an Industrial Diesel Fuel.

The diesel fuel employed had the following analysis data:—

d_{15} 0.829; boiling range 150 to 378°, sulphur content 1.03%.

250 cc. of this diesel fuel were stirred for 30 minutes at 120° C., with 2.48 g. of sodium dispersed in this diesel fuel. After conventional working up, the sulphur content had fallen to 0.79%; even after heating for a longer period, the sulphur content did not fall any further.

However, if 4 g. of bromobenzene were added, the diesel fuel was sulphur-free after the same treatment.

WHAT WE CLAIM IS:—

1. A process for the desulphurisation of liquid hydrocarbons wherein sulphur-containing hydrocarbons are treated with an organo-sodium compound.

2. A process as claimed in Claim 1, wherein the treatment is carried out with the organo-sodium compound and with sodium.

3. A process as claimed in Claim 1 or 2, wherein the organo-sodium compound is formed in the reaction mixture from an organic halogen compound and sodium.

4. A process as claimed in Claim 1 or 2, wherein the organo-sodium compound is formed in the reaction mixture from an organic compound containing an active hydrogen atom linked to a carbon atom and sodim.

5. A process for the desulphurisation of liquid hydrocarbons substantially as described with reference to any of the examples.

6. Liquid hydrocarbons desulphurised by the process claimed in any of the preceding claims.

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